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I.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF SODIUM MALONIC ESTER ON TRIBROMDINITROBENZOL.

By C. Loring Jackson and W. S. Robinson.

Presented June 13, 1888.

In an earlier paper from this laboratory,* the preparation of tribromtrinitrobenzol and its action with ammonia and aniline were described, and the announcement was made that the study of the behavior of this very reactive body would be continued. G. D. Moore and one of us accordingly have taken up the action of sodium malonic ester upon it, in the hope of substituting for each of the bromine atoms the radical of malonic ester, $CH(COOC_2H_5)_2$, and obtaining in this way a substance which might have yielded interesting derivatives. As, however, an entirely different product was the result of the reaction, it seemed wiser to study it with the much more accessible tribromdinitrobenzol, which acted in the same way, and to confine the work on the trinitro compound, which at best can be obtained only with difficulty, to those points in which the two substances showed a different behavior. In this paper, therefore, we give the results obtained up to the present time from the action of sodium malonic ester on tribromdinitrobenzol, which we are obliged to publish now, although in some respects the work is not so finished as we could wish, because the departure of one of us from Cambridge will prevent us from continuing the investigation together.

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* These Proceedings, Vol. XXIII. p. 138.

The most important of these results can be summarized briefly as follows. Sodium malonic ester under the conditions used by us removes from tribromdinitrobenzol only two atoms of bromine, one of which is replaced by the radical of malonic ester, the other by hydrogen, so that the formula of the product is

$$C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2.$$

This substance shows marked acid properties, and, although of a pale yellow color itself, forms salts most of which are dark blood-red; of these the sodium salt was analyzed, and its formula proved to be

$$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2.$$

The yellow copper salt was also analyzed, but proved to be a somewhat complex basic salt. The bromine contained in the substance is easily removed by treatment with aniline, the product being

$$C_6H_2C_6H_5NH(NO_2)_2CH(COOC_2H_5)_2,$$

which also gives a blood-red sodium salt with a formula similar to that of the salt derived from the original substance, but the acid properties of the anilido compound are much less pronounced. When heated with strong hydrochloric acid the bromdinitrophenylmalonic ester gives ethylchloride and a new substance melting at 170°, the analysis of which led to the formula $C_6H_2Br(NO_2)_2C_3H_5O_2$, but the determination of its constitution must be postponed till a later paper.

Action of Sodium Malonic Ester on Tribromdinitrobenzol.

If an alcoholic solution of sodium malonic ester is added to tribromdinitrobenzol (melting point 192°) dissolved in ether, the first drop imparts to the ethereal solution a blood-red color, which increases in intensity as more of the solution of sodium malonic ester is added, and the liquid contains the sodium salt of a new substance, which we prepared in the following way. To an ethereal solution of a weighed quantity of tribromdinitrobenzol we added an alcoholic solution of sodium malonic ester in the proportion of three molecules of the ester to one of the tribromdinitrobenzol. The following were found to be convenient proportions: 20 grm. of tribromdinitrobenzol, 16 grm. of malonic ester dissolved in 100 to 150 c.c. of absolute alcohol and treated with 2.4 grm. of sodium as sodic ethylate. It was not necessary to add the ester gradually, and there was no perceptible evolution of heat during the reaction. The mixture was allowed to stand in a corked flask at ordinary temperatures for three or more hours, and the dark blood-red liquid thus obtained filtered from the precipitate of sodic bromide, which had been deposited, acidified with dilute sulphuric acid, which changed the dark red color to pale yellow, and filtered once more to remove the sodic sulphate formed. The filtrate was then distilled on the water bath until most of the ether had passed over, when the residue in the flask deposited, as it cooled, crystals of the new substance mixed with a large quantity of unaltered tribromdinitrobenzol. The mother liquor from these crystals was allowed to evaporate spontaneously, and left a red or yellow oil mixed with a small additional quantity of the crystals, which were separated from it, and the oil allowed to stand in an open dish for some weeks, when it deposited an additional quantity of the crystals. The crystals, whether obtained by cooling the hot alcoholic solution, or from the oil by long standing in the cold, were purified by dissolving them in a little hot alcohol, and adding a moderately strong aqueous solution of sodic hydrate (the common laboratory solution diluted with its own volume of water), which converted the new substance into its soluble sodium salt, but left the tribromdinitrobenzol unaltered, the red solution was then poured into a large quantity of water, and the tribromdinitrobenzol removed by filtration. If the solid crystals were treated directly with the aqueous solution of sodic hydrate, the tribromdinitrobenzol was left in a form which clogged the filter very badly, whereas when an alcoholic solution was used, as directed above, no difficulty was encountered in the filtration. The red filtrate was acidified with dilute sulphuric acid, and the precipitate purified by crystallization from hot alcohol until it showed the constant melting point 75°–76°. After being dried *in vacuo*, its composition was determined by the following analyses.

I. 0.2061 grm. of the substance gave on combustion* 0.2910 grm. of carbonic dioxide and 0.0602 grm. of water.

II. 0.2013 grm. gave 0.2827 grm. of carbonic dioxide and 0.0511 grm. of water.

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* Care must be taken to heat the substance very gradually, as it shows a tendency to explode in the combustion-tube.

III. 0.1975 grm. gave 0.2780 grm. of carbonic dioxide.*
IV. 0.1926 grm. of substance gave 12.4 c.c. of nitrogen at a temperature of 20° and a pressure of 740 mm.
V. 0.2214 grm. of substance gave by the method of Carius 0.1036 grm. of argentic bromide.
VI. 0.2005 grm. gave 0.0937 grm. of argentic bromide.

	Found.					
	I.	II.	III.	IV.	V.	VI.
Carbon	38.51	38.30	38.38			
Hydrogen	3.24	2.83				
Nitrogen				7.17		
Bromine					19.91	19.88

These results agree about equally well with the numbers calculated from two different formulas, as appears by the following comparison.

	Calculated for $C_6HBr(NO_2)_2C(CO_2C_2H_5)_2$.	Found Mean.	Calculated for $C_6H_2Br(NO_2)_2CH(CO_2C_2H_5)_2$.
Carbon	38.71	38.40	38.51
Hydrogen	2.72	3.03	3.21
Nitrogen	6.94	7.17	6.91
Bromine	19.85	19.89	19.75

The first of these formulas, in which the two atoms of bromine removed from the tribromdinitrobenzol have been replaced by the bivalent radical $=C(CO_2C_2H_5)_2$, seems at first sight the most probable, especially since W. H. Perkin, Jr. and others have observed the strong tendency of sodium malonic ester to react in this way; but although this is the only formula we have been able to find which explains easily the removal of two atoms of bromine in this reaction, we are inclined to reject it in favor of the second one, in which one atom of bromine has been replaced by the univalent radical $-CH(CO_2C_2H_5)_2$, and the other by hydrogen, for the following reasons: —

First, the formation of a sodium salt is hard to reconcile with the first formula, unless, indeed, sodic hydrate was added to it,† giving

$$C_6HBr(NO_2)_2OHCNa(CO_2C_2H_5)_2;$$

but our analyses of the sodium salt, given later in this paper, prove that it contains no hydroxyl, and to make this proof more convincing we prepared the salt for one of our analyses from sodic ethylate, as the radical C_2H_5O-, which in this case would be added instead of hydroxyl, would make a very great difference in the percentage composition of the salt; but this preparation, like the others, gave on analysis numbers corresponding to the formula

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* The water was lost in this analysis.

† Wislicenus, Ann. Chem., ccxlii. 23.

$$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2.$$

Secondly, the ease with which the sodium salt is formed, and with which it is decomposed by an acid giving the original substance, militates against the first formula, as we can hardly suppose that a ring of carbon atoms, such as must be assumed in this formula, would break, when treated with an alkali, and reunite under the influence of an acid in dilute solutions. Finally, we may add that the meta position of the bromine atoms replaced deprives the first formula of any support from analogy.* The principal objection to the formula

$$C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2,$$

which we adopt, is that we cannot account as yet for the formation of such a substance by the reaction of sodium malonic ester on tribromdinitrobenzol. We hope, however, that a careful study of the quantitative conditions of the reaction, and of the oil which is the secondary product, will throw light on this part of the subject; but owing to the departure of one of us from Cambridge, its further investigation must be postponed till next autumn.

The yield was far from satisfactory, 14 grm. of tribromdinitrobenzol after treatment with 12 grm. of malonic ester and 1.7 grm. of sodium, as described above, giving only 4.3 grm. of the bromdinitrophenylmalonic ester instead of the 14 grm. required, if the whole of the tribromdinitrobenzol was converted into the new substance, that is, 30.7 per cent of the theoretical yield. A large amount of the tribromdinitrobenzol was recovered, however, amounting to 5.5 grm., or 39.3 per cent. This leaves 30 per cent unaccounted for, which probably remains dissolved in the oil deposited by the alcoholic mother liquors; but that the dissolved substance is bromdinitrophenylmalonic ester admits of great doubt, as we have not succeeded in obtaining any considerable quantity of this substance from the oil by treatment with aqueous sodic hydrate. This point will be investigated more thoroughly hereafter. We have tried several modifications of the process, in hopes of improving the yield, but none of them have given satisfactory results; if, for instance, the proportion of sodium malonic ester is increased in order to bring more of the tribromdinitrobenzol into the reaction, any gain from this cause is more than compensated by the larger amount of the product taken up by the greater quantity of oil, which is only in part deposited on long standing. Nor was the yield increased by longer standing, or by boiling the materials with a reverse condenser; in this latter case the product came down in an oily form, and with, if anything, rather a smaller yield was much harder to purify.

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* Compare J. Stanley Kipping, Ber. d. ch. G. 1888, p. 32.

Properties of the Bromdinitrophenylmalonic Ester, $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$.

The substance crystallizes in pale yellow flattened needles, or long plates terminated by a single plane, which forms with the sides angles not very far from 90°, but distinctly obtuse and acute. It melts between 75° and 76°, and shows a tendency to explode at high temperatures, so that the heat must be applied carefully when making a combustion of the substance. It is not very soluble in cold alcohol, but freely in hot, more soluble in methyl than in ethyl alcohol, freely soluble in ether, benzol, or glacial acetic acid, even more so in chloroform, moderately soluble in acetone or carbonic disulphide, nearly insoluble in ligroine or water. Strong sulphuric acid in the cold has little action on it, although perhaps a small quantity dissolves; on warming the mixture, complete solution takes place, and addition of water precipitates a solid, which seems to consist principally of unaltered bromdinitrophenylmalonic ester mixed with a small amount of a substance with a higher melting point, probably the compound formed by the action of concentrated hydrochloric acid in sealed tubes (see page 11). Nitric acid, either strong or fuming, dissolves the bromdinitrophenylmalonic ester in the cold, but does not produce any change of color. In this respect, it differs markedly from the corresponding trinitro compound. If the acid solution is warmed, decomposition seems to take place.

The bromdinitrophenylmalonic ester possesses well-marked acid properties, as was to be expected, since it contains a hydrogen atom standing between the two carboxyls of the malonic ester and a phenyl, which, as Victor Meyer * has shown, frequently exercises a negative influence, much heightened in this case by the presence of the two nitro groups. Sodic hydrate in either aqueous or alcoholic solution at once converts it into a soluble red sodium-salt, and the same salt is formed by an alcoholic solution of sodium malonic ester, by sodic carbonate dissolved in water, or by acid sodic carbonate mixed with very dilute alcohol. The aqueous solution of the salt is, however, entirely decomposed by carbonic dioxide, the original substance being precipitated. An aqueous solution of the sodium salt prepared by treating an excess of the original substance with a solution of sodic hydrate gave precipitates with salts of all the common metals except those of the alkalis. Most of these precipitates were red, and among them the following were especially characteristic: —

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* Ber. d. ch. G. 1887, p. 534, 1888, p. 1291 *et seq.*

Baric, strontic, or calcic chloride, dark brick-red.

Magnesic sulphate, rust color.

Zincic acetate, dark chrome-orange.

Basic plumbic acetate, very dark brick-red.

The neutral plumbic acetate gave a yellow precipitate, which turned white when in contact with an excess of lead salt.

Cupric sulphate, dark golden yellow.

Ammonic hydrate also dissolved the substance with a red color, but the salt was decomposed on trying to evaporate off the excess of ammonia on the water-bath, leaving a whitish residue, which seemed to consist principally of the original substance, with a small amount of decomposition product. The substance is in fact easily decomposed by either ammonic or sodic hydrate, and our rather unsatisfactory observations on these reactions will be found on page 11. The sodium salt boiled under a reverse condenser with ethylbromide in alcoholic solution, passed from red through purple, bluish green, green, and brown to reddish yellow; sodic bromide was formed, and the other product was an oily substance, which solidified after some time. It will be studied later. The bromine atom in the bromdinitrophenylmalonic ester seems to be removed with comparative ease. Up to this time, we have studied its behavior in this direction only with aniline (see page 9).

The Sodium Salt $C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2$.

This substance was prepared by dissolving some of the bromdinitrophenylmalonic ester in alcohol and adding a little sodic hydrate, care being taken that the hydrate was not in excess; a little ether was then added, and the mixture evaporated rapidly in a small beaker sunk throughout its whole length in the water-bath. The ether vapor kept the air from coming in contact with the liquid, while the alcohol was being heated to its boiling point. The residue, after all the alcohol had evaporated, was extracted with benzol to remove the excess of the ester, and then dried by gentle warming, and standing *in vacuo* over paraffine and sulphuric acid. These precautions were adopted to avoid the contamination of the substance with the carbonic dioxide of the air. The same substance was obtained when sodic ethylate was used instead of sodic hydrate, and Analysis III. was made with a sample prepared in this way.

I. 0.1950 grm. of the substance ignited with sulphuric acid gave 0.0324 grm. of sodic sulphate.
II. 0.1354 grm. gave 0.0216 grm. of sodic sulphate.
III. 0.1943 grm. gave by the method of Carius 0.0838 grm. of argentic bromide and the filtrate gave 0.0330 grm. of sodic sulphate.
IV. 0.2148 grm. gave 14.3 c.c. nitrogen at a temperature of 25° and a pressure of 759.6 mm.

	Calculated for $C_6H_2Br(NO_2)_2CNa(CO_2C_2H_5)_2$.	Found.			
		I.	II.	III.	IV.
Sodium	5.39	5.38	5.16	5.50	
Bromine	18.74			18.35	
Nitrogen	6.55				7.42

The results of these analyses show that the substance is the normal salt, containing but one atom of sodium, and the important bearing of this point on the determination of the formula of the bromdinitrophenylmalonic ester has been discussed already. (See page 4.)

Properties. — The salt forms a dark blood-red powder, easily soluble in water, alcohol, or ether. From a solution containing much sodic hydrate, the salt can be extracted with ether; but pure water, on the other hand, extracts the salt from its ethereal solution. Its aqueous solution is decolorized by carbonic dioxide bromdinitrophenylmalonic ester being precipitated.

The *copper salt* seemed from its appearance to promise excellent results on investigation, and was accordingly prepared as follows. An alcoholic solution of the bromdinitrophenylmalonic ester was treated with a small quantity of sodic hydrate taking care that the ester was in large excess, and then poured into a volume of water sufficient to precipitate all the unaltered ester; after filtering, an alcoholic solution of cupric chloride was added, and the precipitate washed first with 50 per cent alcohol, then with water, and finally once with hot alcohol; it was then dried *in vacuo.* It is not necessary to protect the salt from contact with the air during its preparation, as it is not perceptibly affected by carbonic dioxide. It gave the following results on analysis.

I. 0.2052 grm. of the salt was treated according to the method of Carius and gave 0.0844 grm. of argentic bromide. The filtrate was freed from argentic nitrate, and the copper precipitated by electricity from a sulphuric of nitric acid solution giving 0.0197 grm. of copper.

II. 0.2073 grm. treated in the same way gave 0.0864 grm. of argentic bromide and 0.0198 grm. of copper.

III. 0.1455 grm. gave 0.0138 grm. of copper.

	Calculated for $HOCu_2[C_6H_2Br(NO_2)_2C(CO_2C_2H_5)_2]_3$.	Found.		
		I.	II.	III.
Copper	9.36	9.60	9.55	9.48
Bromine	17.70	17.50	17.74	

From these results it would appear that the substance is a basic salt, or, at least, that it is not the normal salt, and in spite of its very promising appearance is not fitted to throw light on the nature of the original substance. We have not thought it worth while, therefore, to examine it more carefully. We may add, that the salt changes color from a lighter to a darker yellow soon after it is prepared, which we are inclined to ascribe to the conversion of

$$ClCu_2[C_6H_2Br(NO_2)_2C(CO_2C_2H_5)_2]_3$$

into the corresponding hydroxyl compound by the action of the water in which it is suspended.

Properties. — The copper salt forms an obscurely crystalline precipitate of a golden yellow color, with a very slight greenish tinge. It is essentially insoluble in water, alcohol, or ether, and is a comparatively stable substance, as it seems to be unaltered by exposure to the air, or by heating to 100°. Strong nitric acid, even in excess, decomposes it, setting free the bromdinitrophenylmalonic ester.

Anilidodinitrophenylmalonic Ester,

$C_6H_5NHC_6H_2(NO_2)_2CH(COOC_2H_5)_2$.

This substance was made by mixing the bromdinitrophenylmalonic ester with aniline in the proportion of one molecule of the ester to two of the base. The solid becomes yellow almost immediately, and the action has come essentially to an end after the mixture has stood for a few minutes in the cold. As a measure of precaution, however, we always heated it gently for a few minutes to make certain that all the bromine had been removed. The product was purified by cystallization from alcohol, until it showed the constant melting point 118°, dried at 100°, and analyzed.

I. 0.2104 grm. of the substance gave on combustion 0.4262 grm. of carbonic dioxide and 0.0903 grm. of water.

II. 0.1886 grm. of the substance gave 16.9 c.c. of nitrogen at a temperature of 22° and a pressure of 766.6 mm.

	Calculated for $C_6H_2(NHC_6H_5)(NO_2)_2CH(CO_2C_2H_5)_2$.	Found. I.	II.
Carbon	54.68	55.24	
Hydrogen	4.56	4.77	
Nitrogen	10.07		10.24

Properties. — The anilidodinitrophenylmalonic ester forms flattened needles terminated by one or two planes, which form much more oblique angles with the sides than those which appear in the bromdinitrophenylmalonic ester. It is also found occasionally in star-shaped groups of needles, has a bright yellow color, and melts at 118°. It is only slightly soluble in cold alcohol, much more soluble in hot, but not freely even in this. More soluble in methyl than in ethyl alcohol; soluble in ether, or in carbonic disulphide; freely soluble in benzol, glacial acetic acid, or acetone, very freely in chloroform; essentially insoluble in water or ligroine. The best solvent for it is alcohol. Concentrated hydrochloric acid does not dissolve, or act on it in open vessels, either hot or cold. An aqueous solution of sodic hydrate acts on it in the cold only very slowly and imperfectly, but gives a red solution when boiled with it. In alcoholic solution sodic hydrate converts it into a red soluble salt; the anilido compound therefore still possesses acid properties, but these are much less marked than in the corresponding bromine compound; the negative influence of the dinitrophenyl therefore has been partly neutralized by the introduction of the basic aniline radical C_6H_5NH.

The Sodium Salt $C_6H_2(C_6H_5NH)(NO_2)_2CNa(COOC_2H_5)_2$.

This substance was formed in the same way as the sodium salt of the bromdinitrophenylmalonic ester; that is, by treating an alcoholic solution of the substance with alcoholic sodic hydrate not in excess, evaporating to dryness with a little ether on the water-bath, and extracting the excess of the ester with benzol. It was dried at 100°, and analyzed.

0.1180 grm. of substance gave 0.0194 grm. of sodic sulphate.

	Calculated for $C_6H_2(C_6H_5NH)(NO_2)_2CNa(CO_2C_2H_5)_2$.	Found.
Sodium	5.24	5.32

Properties. — It resembles the sodium salt of the bromdinitrophenylmalonic ester closely in appearance and solubility, but is of a somewhat lighter red. Its solution is decomposed, when treated with carbonic dioxide.

Experiments on the Saponification of Bromdinitrophenylmalonic Ester.

In taking up this subject we considered it necessary to study the action of alkalis on the ester, although, owing to the ease with which the nitro groups are attacked, we had little expectation of reaching satisfactory results. In this we were not deceived, but we think it best to give a brief account of these experiments before describing our more successful work with strong hydrochloric acid in sealed tubes.

A solution of sodic hydrate in water, if boiled with the brom- or anilidodinitromalonic ester, gave a brownish red solution, from which acids precipitated nothing ; but after acidification, and extraction with ether, an unpromising oil was obtained in very small quantity. Cold alcoholic sodic hydrate with the anilido compound gave a somewhat more promising result, but in this case also most of the substance seemed to be decomposed. The bromine compound after standing for two weeks with ammonic hydrate at ordinary temperatures was converted into a similar brown solution, which on acidification gave a resinous brown precipitate and a yellow filtrate, from which ether extracted a substance melting above 200°, ammonic bromide being formed during the process. This is the only one of these products which seems worth further investigation.

Action of Hydrochloric Acid.[*]

When the bromdinitrophenylmalonic ester was heated with strong hydrochloric acid in a sealed tube to 140°–145°, it was decomposed, and upon opening the tube a gas was given off in tolerable quantity, which burnt with a green-bordered flame, and was without doubt ethylchloride. About one gram of the substance and 20 c.c. of common strong hydrochloric acid were used in each tube, and the temperature should not be allowed to go above 150°, as in this case an impure product was the result. If proper care was used in the heating, the tube contained crystals, or a clear liquid, from which crystals were deposited after the pressure was relieved; these were filtered out and the filtrate thrown away, as it gave almost no residue on evaporation, and no extract when shaken with ether.

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[*] All our work on this part of the subject must be regarded as preliminary.

The crystals were purified by crystallization from dilute alcohol (three parts of water to one part of alcohol). If the temperature was kept below 150°, the product was nearly pure, as it came from the tube; but if it had risen above this point, a small quantity of a lower melting substance was formed, which it was almost impossible to remove with dilute alcohol. In this case the best plan was to dissolve the substance in chloroform, when the impurity separated at first as a pasty mass, leaving the principal product in solution, which after one crystallization from dilute alcohol showed the constant melting point 170°. It was dried at 100°, and analyzed with the following results.

I. 0.1307 grm. of substance gave on combustion 0.1634 grm. of carbonic dioxide and 0.0278 grm. of water.
II. 0.2162 grm. of substance gave 0.2688 grm. of carbonic dioxide and 0.0495 grm. of water.
III. 0.2136 grm. of substance gave 18.3 c.c. of nitrogen at a temperature of 22° and a pressure of 760 mm.
IV. 0.1197 grm. gave 10.2 c.c. of nitrogen at a temperature of 28° and a pressure of 762.9 mm.
V. 0.2212 grm. of substance gave by the method of Carius 0.1365 grm. of argentic bromide.
VI. 0.2120 grm. gave 0.1275 grm. of argentic bromide.

	Found.					
	I.	II.	III.	IV.	V.	VI.
Carbon	34.10	33.91				
Hydrogen	2.37	2.54				
Nitrogen			9.48	9.39		
Bromine					26.29	25.59

These numbers agree tolerably well with those required for the formula $C_6H_2Br(NO_2)_2C_3H_5O_2$.

	Calculated.
Carbon	33.86
Hydrogen	2.19
Nitrogen	8.77
Bromine	25.08

But the formula cannot be considered definitely established, until we have supported our analytical results by a careful study of the derivatives of the substance.

Properties. — The substance crystallizes from dilute alcohol in yellowish white narrow plates, sometimes half a centimeter in length, which are made up of needles attached to another needle acting as a midrib at very acute angles, giving an exact imitation of a feather or more commonly of one side of a feather; this form is very characteristic, and, when not so well developed, the substance can be recognized by the formation of narrow plates, usually smooth on one side and rather irregularly serrated on the other, or upon the ends. The plates often occur in radiating groups, the members of which form very acute angles with each other. From methyl alcohol or ether it crystallizes in very slender needles, much branched at very sharp angles, often forming circular groups resembling certain seaweeds. It melts at 170°, is not very soluble in cold alcohol, freely in hot, more soluble in methyl than in ethyl alcohol, freely soluble in glacial acetic acid or acetone, tolerably soluble in ether, slightly soluble in benzol either cold or hot, or in carbonic disulphide, slightly soluble in cold chloroform, more soluble but not freely in hot, nearly insoluble but not quite so in cold water, more soluble but still very slightly in hot, essentially insoluble in ligroine. The best solvent for it is chloroform, or a mixture of alcohol and water. Its behavior with alkalis is very characteristic. If a drop of an aqueous solution of sodic hydrate is added to the substance dissolved in alcohol, the solution takes on a dark but brilliant Prussian green color. This solution becomes colorless on addition of hydrochloric acid, but turns green again on addition of sodic hydrate. The green alcoholic solution, if allowed to evaporate spontaneously, leaves a brownish yellow residue, and a solution of the same brownish yellow color is obtained if an *excess* of sodic hydrate is added to the original substance. If the yellow solution, in whichever way prepared, is acidified with hydrochloric acid, it loses its color, and oil-drops are precipitated, which solidify in time. These dissolve in sodic hydrate with a brownish claret * or pale magenta color, which is unaltered by dilution with water, but turns green on addition of alcohol. The substance melting at 170° is not affected by an aqueous solution of sodic carbonate. The further study of these interesting reactions has been broken off by the summer vacation, but will be continued in this laboratory in the autnmn.

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* A somewhat similar change of color was observed during the action of ethylbromide on the sodium salt of the bromdinitrophenylmalonic ester.